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TRANSPORT PROCESSES IN CERAMIC OXIDES

Order No. 1130, Program Code No. 8D10

AVSD-0067-70-CR

Semi-Annual Technical Report

16 June 1969 - 15 December 1969

Contract No. DAHC 1568C0296 (16 June 1969)

Expiration Date: 15 June 1970

Project Scientists: T. Vasilos - 617-452-8961
B.J. Wuensch
P.E. Gruber
W.H. Rhodes

Contractor: Avco Corporation
Systems Division
Lowell, Massachusetts 01851

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ABSTRACT

Progress is described in a program intended to clarify the nature of mass transport in MgO, a ceramic oxide. The objectives of the program are to (1) prepare single crystals of purity and perfection superior to those presently available, (2) develop techniques permitting study of stable isotope diffusion and apply them to cation self-diffusion in MgO, and (3) extend measurement of impurity cation and cation self-diffusion coefficients to temperatures as close to the melting point of MgO as possible, in an attempt to reveal a region of intrinsic diffusion.

Measurements of cation self-diffusion rates obtained for MgO are tentatively represented by a pre-exponential term, D_0 , equal to $3.5 \cdot 10^{-3} \text{ cm}^2/\text{sec}$ and an activation energy of 3.13 eV, confirming a surprisingly large value reported elsewhere on the basis of data obtained over a very limited temperature range. Diffusion rates in high purity crystals are smaller by a factor of 2, and transport is interpreted as extrinsic. Measurements of Ni^{2+} diffusion in MgO have been extended to 2460°C . Data agree well with an extrapolation of measurements performed at lower temperatures. Surprisingly, diffusion in high purity crystals is more rapid. At 2460°C there is indication of a possible change in the mechanism of diffusion.

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I. INTRODUCTION

Many properties of solids are diffusion controlled. Ionic conduction, creep, sintering, and solid state reaction are but a few examples of processes for which migration rates of the constituent ions may be the rate-limiting step. Efforts to predict and interpret the rates of such processes have prompted a number of studies of mass transport in single crystals. Simple ionic materials, such as the alkali halides, are fairly well understood. Reliable estimates, both theoretical and experimental, are available for the energies of formation and migration of defects.

Extension of this understanding to oxides has not been straightforward. Theory has been generally unsuccessful in providing estimates of defect formation energies. The higher melting points of these materials causes the preparation of single crystals to be difficult. Furthermore, the higher defect formation energies in oxides permit these materials to contain only very low concentrations of impurities if the intrinsic transport properties of the solid are not to be masked by chemically-created defects. Very few oxides are available with a quality which meets this requirement. To detect intrinsic transport behavior in crystals of marginal purity, one would ordinarily perform measurements at temperatures as close as possible to the melting point of the material. Such temperatures for oxides are accessible only with great difficulty.

The present program is concerned with a single material--magnesium oxide. This material is of considerable technological importance (e.g., refractories, transparent ceramic armor and high temperature infrared applications). MgO has the rock salt structure common to most of the alkali halides, and therefore would appear to be an oxide to which the understanding acquired for simpler ionic materials might be readily extended.

Single crystals of MgO, although of questionable purity and perfection, have long been available. A sizeable portion of the literature on mass transport in oxides has, therefore, been concerned with this material. Most of these studies, however, have provided little insight into the fundamental nature of the transport process, and the experimental situation is far from clear.

Self-diffusion coefficients have been determined for both Mg^{2+} and O^{2-} in single crystal $\text{MgO}^{(1,2)}$ in temperature ranges of $1400^\circ - 1600^\circ\text{C}$ and $1300^\circ - 1450^\circ\text{C}$, respectively. The Mg^{2+} diffusion data could be represented by a single activation energy for diffusion equal to 3.43 eV in the temperature range studied. This result has been interpreted as representing intrinsic diffusion since it can be expressed as the sum of a reasonable energy (ca 0.9 eV) for ion migration and half of the theoretically estimated energy⁽³⁾ for Schottky defect formation (2.5 eV). The O^{2-} self-diffusion data could be represented by an activation energy of 2.71 eV. This result was interpreted as extrinsic diffusion by virtue of a negative entropy of activation and an activation energy which was small compared with that observed for Mg^{2+} diffusion.

Diffusion data have also been obtained for a large number of impurity cations in single crystal MgO: Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Zn^{2+} , Be^{2+} , Ca^{2+} , and Ba^{2+} (4-11). The activation energies for diffusion for most of these cations are close to 2 eV despite the fact that many have radii which are close to that of Mg^{2+} . The fact that these energies are less than half the estimated energy for Schottky pair formation, plus the fact that the pre-exponential terms, D_0 , observed for impurity diffusion are all small (ca $10^{-5} \text{ cm}^2/\text{sec}$) strongly suggests that all of these results represent extrinsic behavior. The purity of the crystals which were employed also

suggests this. If the activation energy for Schottky pair formation is of the order of 5 eV, a few hundred ppm of aliovalent impurity would be sufficient to cause transport in MgO to be extrinsic for all temperatures up to its melting point. The MgO crystals employed in most studies contain in excess of a thousand ppm impurity.

The conclusion that extrinsic diffusion has been measured in all impurity transport studies is difficult to reconcile with the much higher activation energy observed for Mg^{2+} self-diffusion. All measurements were made in a similar temperature range, and many of the impurity cation studies were conducted with crystals obtained from the same source as those employed in the self-diffusion measurements. The activation energies for impurity ion diffusion are much larger than the 1 eV migration energy suggested by the self-diffusion studies. These energies, therefore, cannot represent the energy for ion migration alone. No study of diffusion in MgO has yet revealed an increase in activation energy at higher temperatures which would permit unequivocal identification of regions of intrinsic and extrinsic transport behavior.

The present program is intended to clarify the nature of mass transport in MgO, and to permit an evaluation of the energy of defect formation in this material. In view of the above discussion, the outstanding problems appeared to be: preparation of single crystals of improved perfection and purity, re-examination of the unique results obtained for Mg^{2+} self-diffusion, and extension of transport measurements to much higher temperatures. Accordingly, the program consists of four main efforts;

1. Attempts are being made to synthesize single crystal MgO of purity superior to that presently available. Chemical vapor deposition techniques seem particularly promising in this

area, and exploration of these methods constitute the major portion of this effort.

2. Crystal surface preparation and characterization in relation to transport measurements.
3. Mg^{2+} self-diffusion rates are being determined over a wider range of temperatures than previously was possible. Such measurements are complicated by the lack of a suitable radioactive tracer. Mg^{28} , the longest-lived radioisotope, has a half-life of only 21.3 hours, and this has restricted previous measurements to high temperatures. This difficulty will be circumvented through measurement of diffusion rates of a stable isotope of Mg. A mass spectrometer is to be used in establishing concentration distributions of the isotope.
4. Mg^{2+} self-diffusion measurements and impurity cation diffusion measurements are to be extended to much higher temperatures than previously investigated. Diffusion rates in MgO have not been determined at temperatures above 1850°C (0.66 of the melting temperature of MgO). Such measurements are to be extended to temperatures at least as high as 2500°C (0.9 of the melting point) in an attempt to reveal a region of intrinsic diffusion.

Progress to date in each of these areas is described in subsequent sections.

II. CRYSTAL GROWTH

Experiments have continued to improve the technique, established in the first year's effort, for crystal growth by chemical vapor transport of MgO in HCl. Considerable effort has been devoted to developing a new

transport geometry which has recently shown marked improvement in deposition rate.

2.1 Experimental

Earlier crystal growth experiments⁽¹²⁾ demonstrated the possibility of preparing single crystal magnesia by chemical transport in HCl. The transport geometry evolved from this work consisted of a platinum crucible with the source MgO in the bottom and the seed crystal over a hole in the crucible cover. The crucible, suspended in a quartz tube with a reduced atmosphere of anhydrous HCl, was heated by means of an R.F. coil around the quartz tube. The positioning of the crucible was such that a slight temperature difference could be maintained between the source MgO and the seed crystal to provide the transport potential. (Details of this system appear as Figure 5 of Ref. 12.)

Although epitaxial deposits on MgO seed crystals were obtained with this geometry, there were inherent disadvantages. The major difficulty appeared to be the poor closure provided for the seed crystal over the deposition opening in the crucible cover. As a result, considerable MgO was deposited as a fine powder on the cool-walls of the enveloping quartz tube. Thus, a very large amount of source material had to be placed in the crucible initially which, as it was consumed, resulted in changes in the diffusion distance and temperature gradient.

To overcome this difficulty, it was decided to develop a transport geometry incorporating the source and seed within a tightly closed crucible. A number of variations were tried with limited success but which resulted in the gradual evolution of the present scheme. The apparatus now being used, shown in Figure 1, is similar to that employed previously⁽¹²⁾ differing only in the arrangement of the crucible. Two distinct advantages are

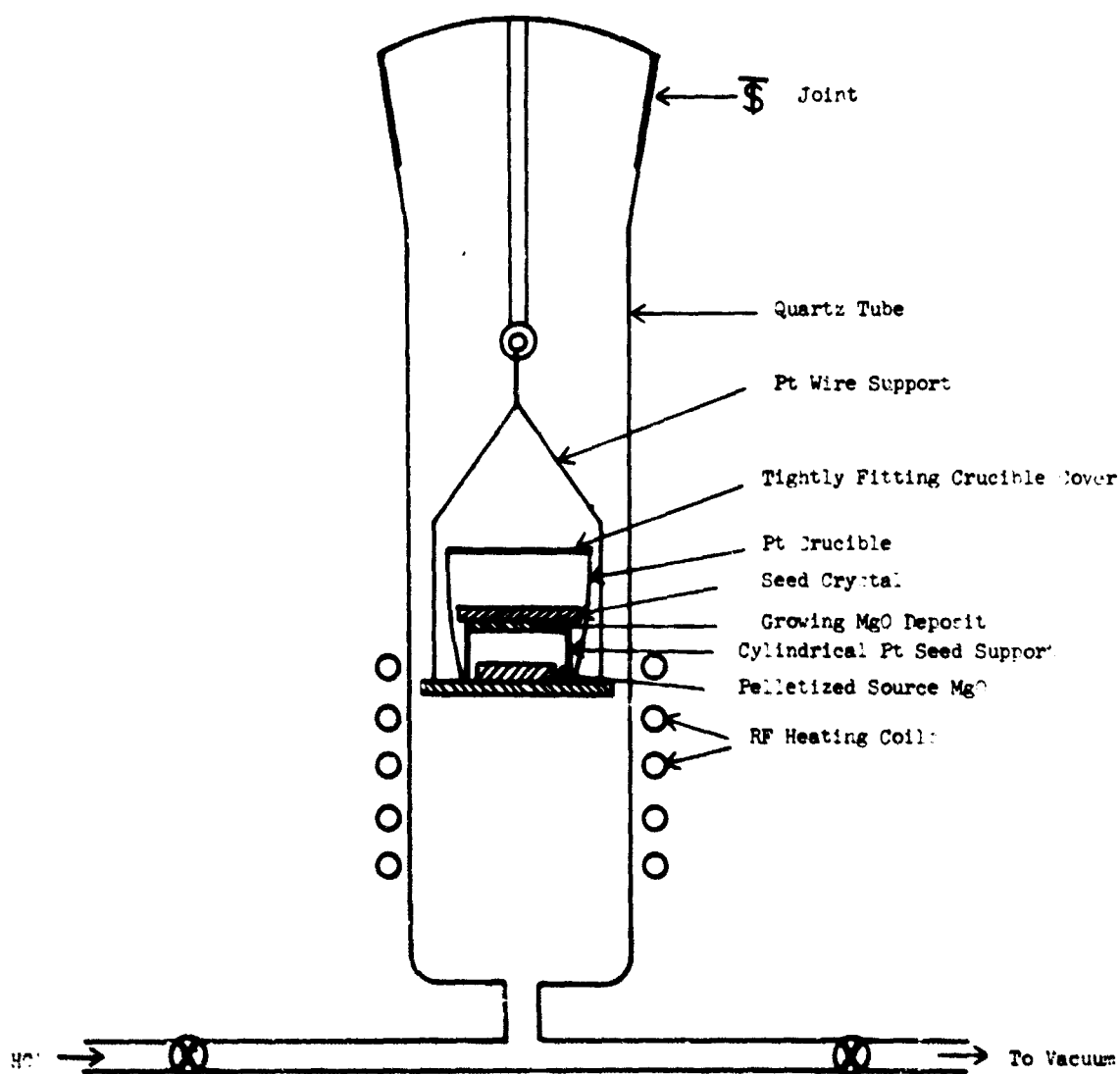


Figure 1.

Schematic of Latest Apparatus for MgO Chemical Transport in HCl
Employing a Closed Crucible.

realized with this apparatus. Loss of MgO from the crucible can be kept very low because of the tightly fitting crucible cover. The shorter diffusion path possible with this closed crucible geometry can result in higher deposition rates.

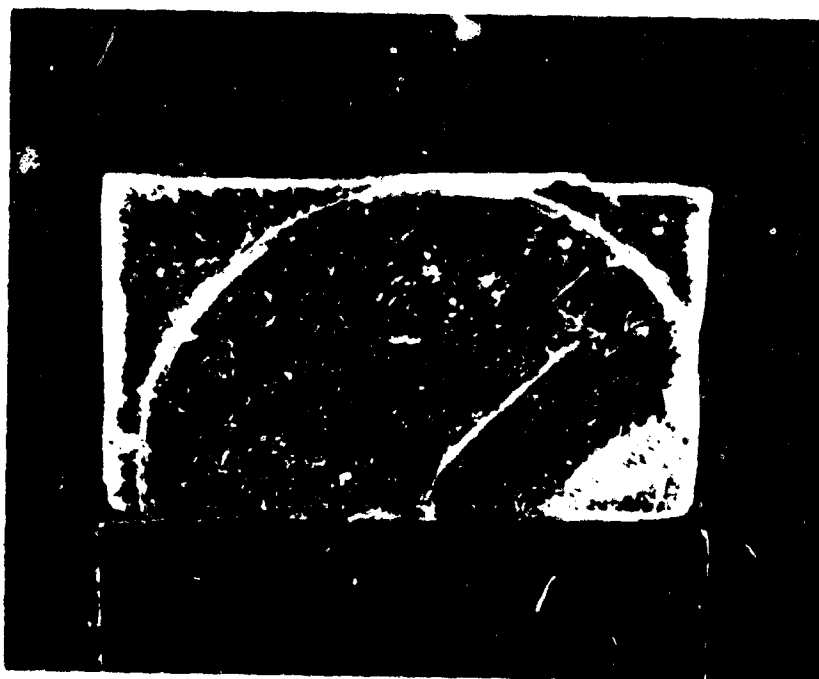
The experimental procedure closely follows that described previously⁽¹²⁾ with a few changes. A platinum crucible is charged with a pellet of about 500 mg of MgO powder. This pelletizing was adopted as a means of eliminating contamination of the seed crystal with MgO dust which tended to be distributed around the interior of the crucible when the R.F. field was first applied. The MgO seed crystal, cleaned and etched in hot H_3PO_4 was then centered on the hollow cylindrical platinum support above the MgO source pellet. A specially made tightly fitting platinum cover is used to close the crucible which is then suspended in a quartz tube such that only the lower portion of the crucible is in the field of the R.F. coils. The exact positioning of the crucible in the coil was a matter of considerable experimentation before a position providing desirable results was found, and is shown in Figure 1. The quartz tube containing the charged crucible was then evacuated to approximately 10^{-6} torr while the lower portion of the crucible containing the source MgO was heated to 1000°C . With the system thus "baked-out," anhydrous HCl was admitted to the tube to a desired pressure. The HCl pressure is set at either 10 or 40 mm Hg and good deposits have been obtained at both settings. The 40 mm level has given predictably faster deposition rates, however, and has been used exclusively in the most recent work. With this higher HCl pressure, condensation of MgCl_2 on the inner surface of the quartz tube was observed. If allowed to continue long enough, the resulting depletion of chloride was the apparent

cause for changing the preferred mode of growth from (100) to (111) before ultimately choking off all transport of MgO. To correct this, the exterior of the quartz tube was wrapped with heating tape which, it was determined, when held at about 80°C virtually prevented all MgCl_2 condensation. With these preparations completed, the R.F. heater is adjusted so that the base portion of the crucible is 1000°C. Since the upper portion of the crucible is above the R.F. field, its temperature is well below incandescence. This resulting thermal gradient also provides the chemical potential for the transport of MgO.

2.2 Results

About seventy attempts with variants of the closed crucible geometry were tried before good epitaxial deposits were obtained. The reasons for the failures can only be conjectured but the results were generally either polycrystalline or discolored deposits or no deposits at all. Eight deposits about 300 to 500 microns thick have been made recently after the favorable experimental conditions discussed above were established. Thus, the primary emphasis of this work, which has been to determine the best conditions for crystal growth, has apparently been accomplished. The effort will now be shifted to improving the quality of the crystal growth. The quality of the deposits resulting from these last experiments has been examined as a guide for future work.

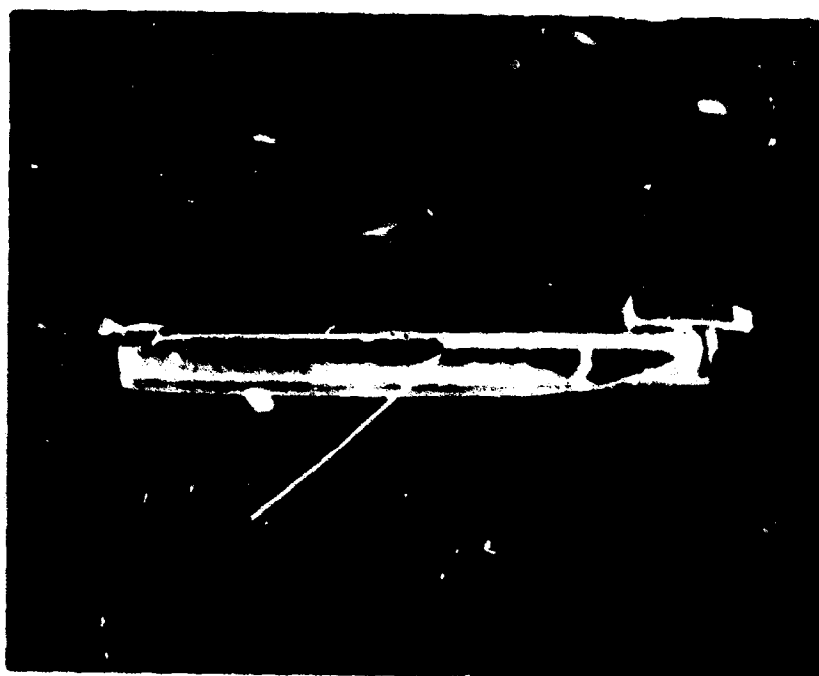
A typical deposit which has been cleaved, normal to its growth direction, can be seen in Figure 2. The deposited MgO before cleaving is circular, as a result of its growing inside the cylindrical seed crystal support (see Figure 1). The rectangular portion, seen in Figure 2, is the remains of the seed crystal. The sample has been tilted to about 30° for



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4X

Figure 2. Cleaved Sample (21) Showing Deposit (Circular) and Substrate (Rectangular). (Inclined 30° to focal plane of camera.)



2

4X

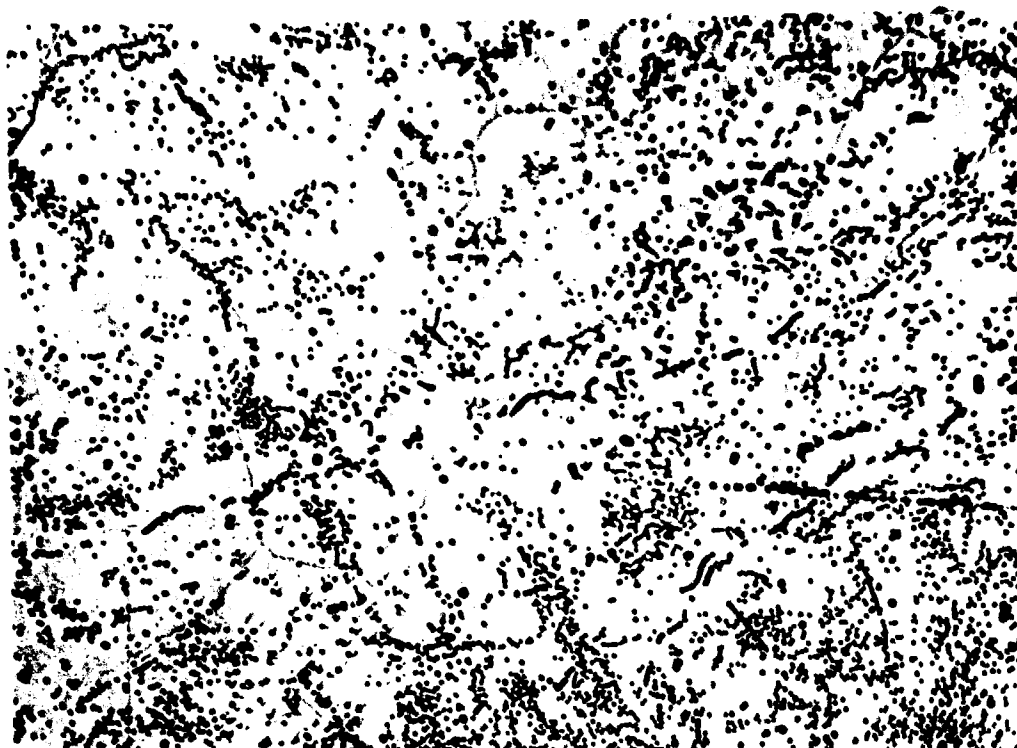
Figure 3. Cleaved Sample (Sample 2) Showing Partial Perimeter of Deposit (inter right).

this photograph to better show the relation of deposit and substrate. A portion of the deposit separated from the substrate when it was cleaved. This separation is more apparent on a picture of the cleavage face of the same sample (see arrow, Figure 3).

The deposit shown in Figure 2 required 23 hours to form. Since its thickness is over 500 microns, the average deposition rate is in excess of 20 microns/hour. This is a significant increase over previously measured rates. Shorter deposition times result in even higher average rates, which may be explained by the chloride depletion mentioned earlier.

Sample 96 was etched for 15 minutes at room temperature in a solution comprised of a 5:1:1 volume ratio of saturated NH_4Cl , concentrated H_2SO_4 , distilled H_2O to bring out dislocations. Figure 4 shows the etched surface of the deposit which has a dislocation density of $2.5 \times 10^6 \text{ cm}^2$. This is higher than desirable but may well be a result of the very high number of dislocations on the growth surface of the seed crystal. Figure 5 shows the surface of the substrate immediately adjacent to the deposit, which has $1.8 \times 10^7 \text{ dislocation/cm}^2$. Substrate dislocations can probably be greatly reduced during preparation of the seed crystal by more extensive phosphoric acid etching or thermal etching.

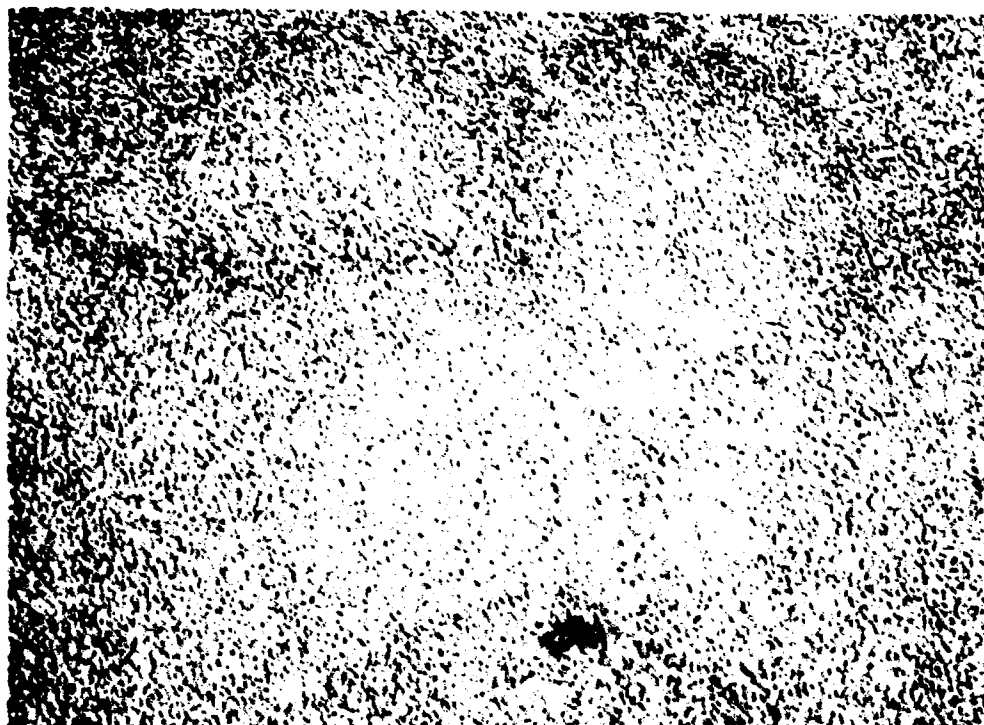
Careful examination of the cleavage face of sample 92 shows numerous cleavage steps running from the substrate into the deposit. This is a strong indication that the growth was epitaxial. A von Laue reflection pattern further supports this conclusion. In this case, the sample was aligned such that the cleavage surfaces on the edges of the substrate were horizontal and vertical and the radiation (unfiltered copper, 40 kv, 20 ma) incident in the $[100]$ direction. The resulting pattern (Figure 6) which, as will be demonstrated can be ascribed largely to the deposit,



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Figure 4. Surface of Deposit Showing Etch Pits.



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Figure 5. Surface of Substrate Immediately Adjacent to Deposit Showing Etch Pits.

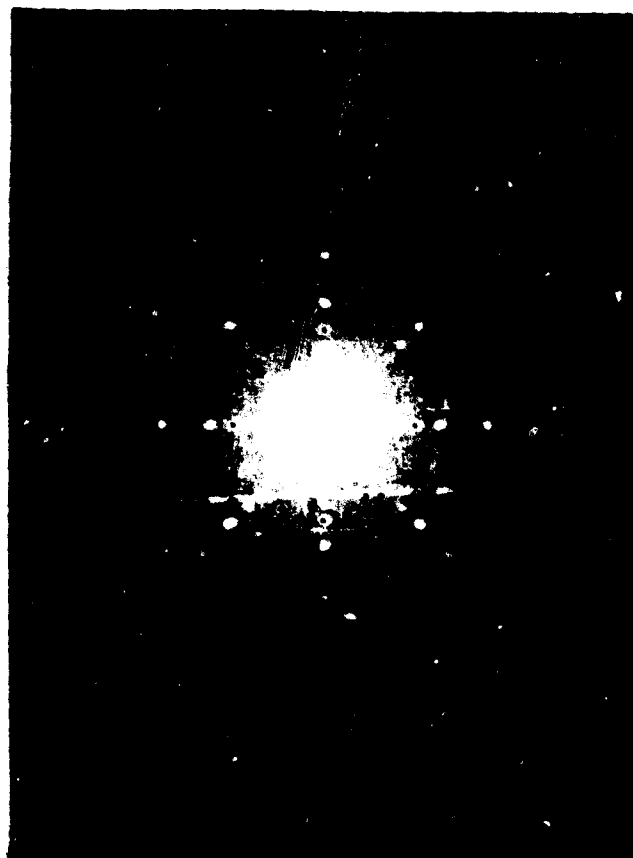


Figure 6. von Laue Reflection Pattern of Sample 92.

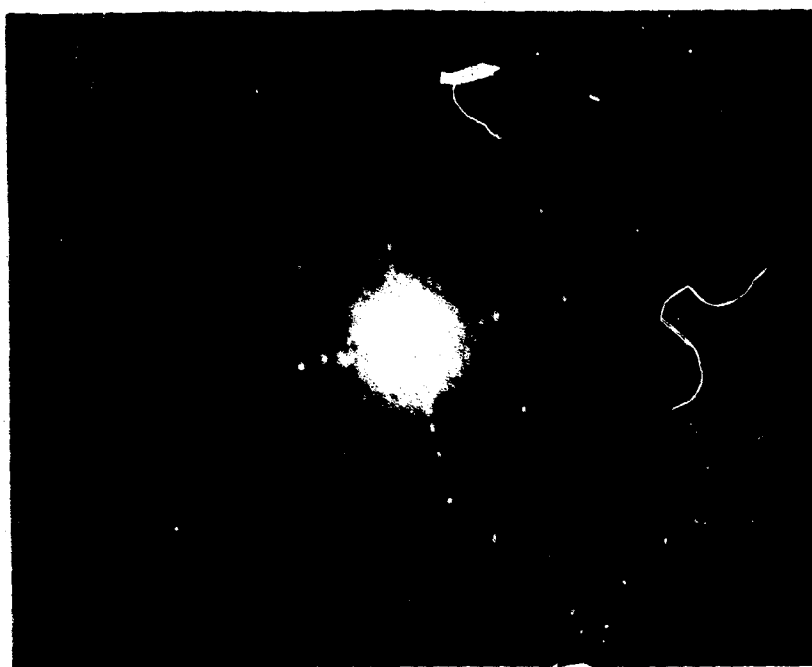


Figure 7. von Laue Pattern from Fragment. Simulating
Circle 1 with 1.5 Microlayers.

corresponds to a (100) face, showing that the deposit is a single crystal and has the same orientation as the substrate. To demonstrate the relative influence of the substrate and deposit in this von Laue pattern, a sample was prepared from two cleavage fragments, simulating the substrate and deposit of sample 92, but with a 14° misalignment of the fragment representing the deposit. The resulting von Laue pattern shown in Figure 7 shows only a very weak pattern for the "substrate", while the stronger pattern indicates that most of the reflections come from the misaligned "deposit". The same contribution from substrate and deposit can be ascribed to the pattern of sample 92 (Figure 6). That only one pattern can be seen in the reflections from sample 92 again demonstrates that the substrate and deposit have the same orientation.

Chemical analysis for impurities known to be present in the source MgO plus platinum and chlorine were performed on the deposit which was cleaved from sample 94. Emission spectrometry was used for all cations except calcium which was determined by atomic absorption spectrometry. Chloride analysis was made by mercurimetric titration which has a sensitivity of ppm⁽¹³⁾. Table I is a comparison of the impurities in the source MgO and those found in the deposit from sample 94.

The substantial reduction of Ca, Mn, and Si, the reasonable low Pt contamination and the absence of Cl in the deposit is encouraging; especially since the emphasis in these experiments was primarily centered on demonstrating the closed crucible geometry. Techniques of purification of the source MgO discussed in the effort of the previous year⁽¹²⁾ will be used to further reduce these impurities levels.

TABLE I
Impurities Found in Source MgO and
Deposit 94 (ppm)

<u>Element</u>	<u>Source</u>	<u>Deposit</u>
Al	100	124
B	100	nil
Ca	1000	165
Cr	nil	-
Cu	100	92
Fe	100	96
Mn	100	nil
Pt	-	9
Si	1000	125
Ti	20	17
Zn	nil	-
Cl	-	nil

III. SURFACE PREPARATION AND DISLOCATION CONTENT

One boundary condition for a diffusion experiment is the establishment of a plane of zero or known concentration at time zero. Thus, a surface must be prepared whose roughness and deviation from flatness is small with respect to the total diffusion profile and ideally small with respect to the first few sections. In the earlier work⁽¹²⁾, it was established that this flat surface was best prepared by mechanically polishing. This, of course, introduced heavy dislocation damage. The dislocation concentration of a polished MgO crystal was determined to be approximately 8×10^7 d/cm².

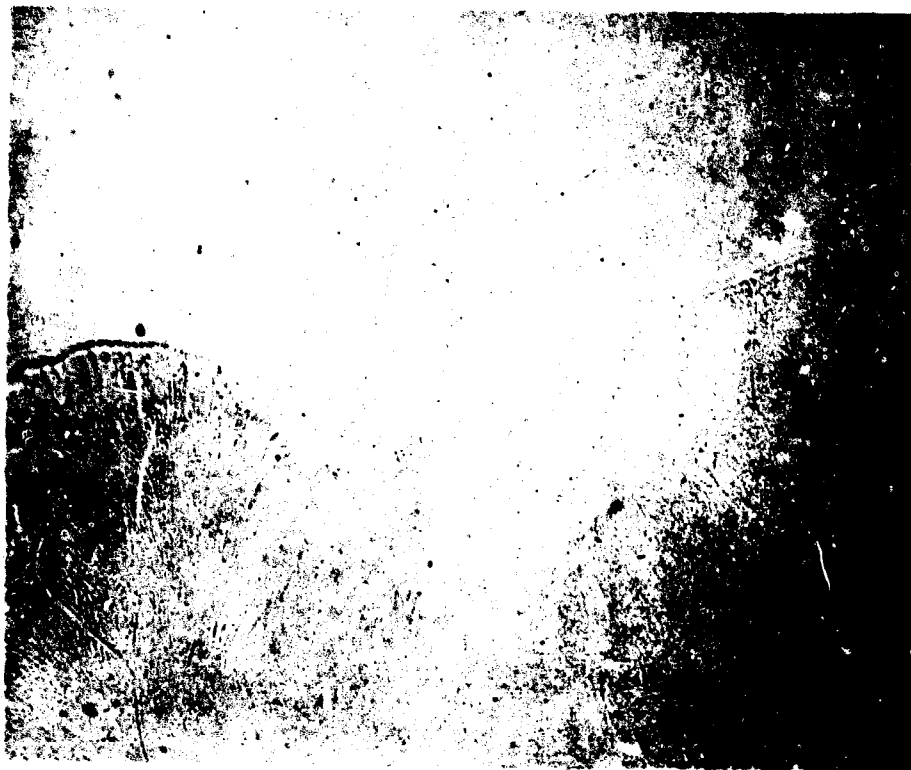
It was decided that due to the known effects of dislocations on self-diffusion in SiTiO₃^(14,15), NaCl⁽¹⁶⁾, and Al₂O₃⁽¹⁸⁾, it would be desirable for this study to have starting crystals of (1) known dislocation concentrations, (2) as low as possible dislocation concentration, and (3) uniform concentrations throughout the thickness of the expected penetration. Therefore, it was desirable to eliminate the damaged region of the polished crystal and to that purpose annealing experiments were conducted in the previous period. After much experimenting, a procedure was developed for reducing the surface concentration to 0.6 to 2.1×10^7 d/cm² while maintaining the flat surface, but this was still about two (2) orders of magnitude above the native grown-in dislocation concentration. It was also determined that the damaged layer was about 40 microns deep, thus the diffusion profile could well encounter regions of vastly different concentration.

Chemical polishing with hot phosphoric acid is known to remove large quantities of MgO. In fact such a treatment followed by etching for dislocations was the technique used to determine the native dislocation concentration. Chemical polishing usually resulted in wavy surfaces which

were thought to be unsuitable as a starting surface for the diffusion penetration because of the contour. However, from a dislocation concentration standpoint, the surface was highly desirable; thus, it was decided to conduct experiments to determine whether or not a surface of suitable flatness could be generated by the hot phosphoric chemical polishing.

A number of experiments were performed by rotating a polished MgO crystal in close proximity to a flat glass plate which was immersed in the hot phosphoric acid. This approach resulted in sufficient chemical polishing to remove the damaged layer, but marked surface waviness was apparent. Next a crystal was immersed in the 190°C phosphoric and rubbed against the flat glass plate using a figure eight motion. Two minutes of polishing resulted in a surface that appeared very flat. Nine microns of material were removed from each side by this polishing which was not enough to penetrate the entire damaged layer, (estimated to be 40 μm deep). However, the dislocation concentration was within the 10^6 d/cm^2 range which is a definite improvement over annealing.

Polished static control samples were run along with the rotating crystal experiments. Several of these appeared quite promising, and more extensive testing was conducted on static and low velocity chemical polishing (rotating crystal experiments were dropped). It was found that 10 minutes with slow agitation in 185°C phosphoric acid removed 40 microns from each side. Although the best cycle to date does not reproduce the flatness of the mechanically polished surface, characterization of the surface was undertaken to determine whether or not it would satisfy the requirements. Figure 8 illustrates the appearance of the chemically polished surface. Very few pits were noted although some surface waviness was noted. Placement of the surface against an optical flat revealed



5211-2

250x

Figure 8. Chemically Polished Norton MgO Single Crystal
(Sample No. ()

(in monochromatic light) an irregular 12-band interference pattern indicating that the entire surface was flat to within 3.5 microns. Tallysurf (diamond stylus) traces demonstrated that the short range surface finish was 0.3 microinch (0.0075 microns) and long range contours had an elevation variation of ± 30 microinches (0.75 microns). Thus, the two methods of measuring flatness agree within a factor of five. Since the section thickness is from 2-3 microns for the shortest diffusion profile measured, this flatness may be adequate as these height differences should be removed within the first two sections. It is thought that further improvement in flatness can be made by a combination of efforts to improve the flatness of the mechanically polished starting surface and slight variations of the chemical polishing treatment.

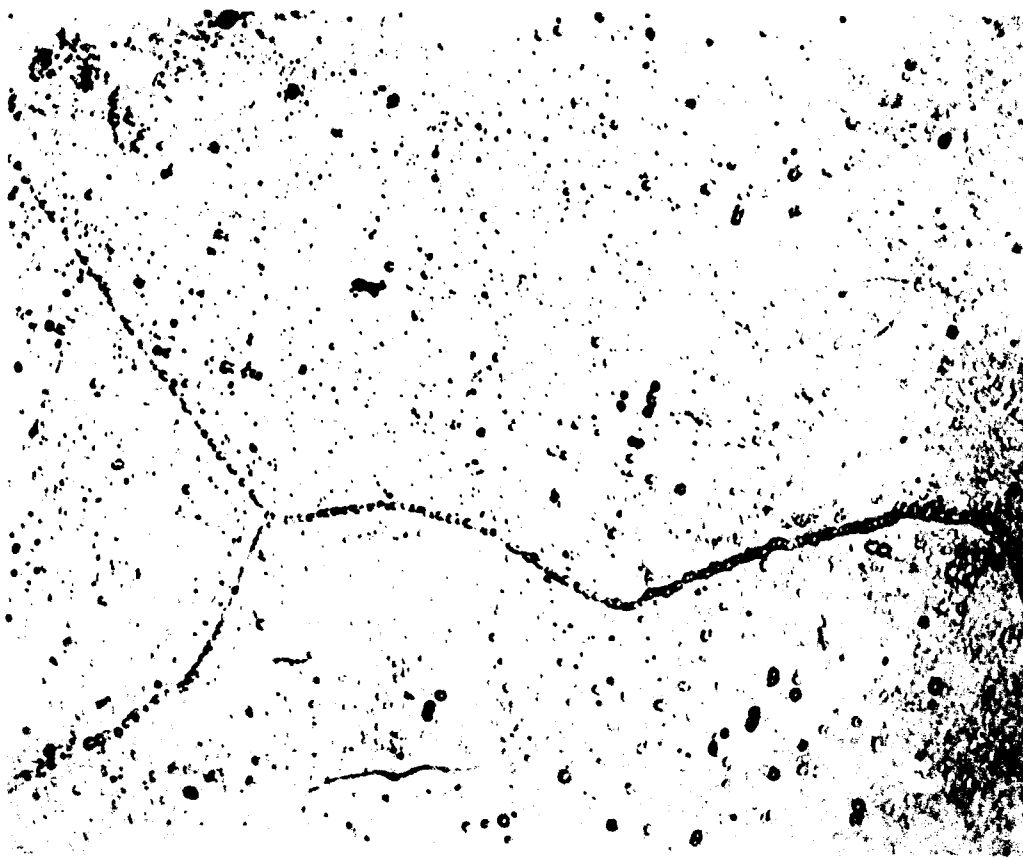
Several specimens given this chemical polishing cycle were etched to measure dislocation content. Figure 9 shows an area near the edge of one crystal given a 10-minute polish. Some waviness is apparent, and this occurred during chemical polishing. Also apparent are several glide bands which are a result of damage on the adjacent surface. Neither of these features would interfere with a diffusion experiment because a 2 mm slice perpendicular to the diffusion plane is removed after the diffusion anneal, but prior to the sectioning of the couple for analysis. The central more uniform region of the crystal possessed the dislocation structure shown in Figure 10. The dislocation concentration was $1.53 \times 10^5 \text{ d/cm}^2$ which was within the range previously measured⁽¹²⁾ for the native dislocation content of Norton-type crystals. This fact plus the lack of regular slip traces led to the conclusion that the chemical polishing cycle successfully removed the damaged layer.



5211

250x

Figure 9. Edge of Chemically Polished Norton Crystal After Etching for Dislocations (Sample No. 6)



5211-1

250x

Figure 10 . Center of Chemically Polished Norton Crystal After Etching for Dislocations (Sample No. 6).

IV. MAGNESIUM SELF-DIFFUSION IN SINGLE CRYSTAL MgO

4.1 Approach to the Problem

Previous studies of magnesium self-diffusion have been hampered by the lack of a convenient radioisotope. The longest lived radioisotope, Mg^{28} , has a half-life of only 21.3 hrs. This had restricted measurements to a narrow range of high temperatures within which isotope penetrations of an extent suitable for mechanical sectioning could be produced by a diffusion annealing of short duration. To circumvent this limitation, diffusion of a stable isotope is being studied in the present investigation. Magnesium has three stable isotopes: Mg^{24} , Mg^{25} , and Mg^{26} , with natural abundances of 78.70%, 10.13%, and 11.17%, respectively. Mg^{26} has been selected for use as a tracer in order that the maximum resolution relative to the most abundant isotope may be obtained. The isotope is obtained from the Oak Ridge National Laboratory as a fine grained MgO powder enriched to 98.78% Mg^{26}O . The isotope is applied to a prepared surface of a MgO host crystal in one of two fashions described below. The specimen is subjected to a diffusion annealing in an argon atmosphere for a predetermined time and temperature. Following the annealing, the distribution of isotope in the sample is determined by removing thin (2 to 3 microns) sections by mechanical grinding. The isotopic composition of each section is determined with the aid of mass spectrometry. A diffusion coefficient may be computed from the concentration distribution so determined.

4.2 Specimen Preparation

Diffusion coefficients are readily computed from an experimentally measured concentration distribution provided that the conditions under which the sample has been prepared are chosen such that a simple solution to the diffusion equation applies. Two types of specimens have been

employed in the present study. Their convenience for use depends on the vapor pressure of MgO at the temperature being examined.

In a first type of specimen an exposed surface of MgO single crystal is placed over a well cut in a single crystal of the same material as the host crystal. Mg^{26}O powder is placed in the well. The surface of the host crystal is thus in equilibrium with a vapor of the isotope during the course of the diffusion annealing. The resulting concentration C , following an annealing of time, t , is given by

$$(C - C_0) = C_s - C_0 \operatorname{erfc} x (4Dt)^{-\frac{1}{2}}$$

where C_0 is the natural abundance of Mg^{26}O in the sample (11.17%), C_s is the surface concentration, x is penetration into the specimen, D is the diffusion coefficient, and erfc is the complementary error function. A plot of $\operatorname{erfc}^{-1} (C - C_0)/(C_s - C_0)$ is therefore linear and has slope given by $(4Dt)^{-\frac{1}{2}}$.

In a second type of specimen, a film of isotope is initially deposited between two prepared surfaces of host crystal. The concentration distribution for this "sandwich" specimen is given by

$$(C - C_0) = S (4Dt)^{-\frac{1}{2}} \exp -x^2 (4Dt)^{-1}$$

where S is the initial amount of solute per unit area. A plot of the logarithm of $(C - C_0)$ as a function of penetration squared is therefore linear, and has slope given by $(4Dt)^{-1}$.

The two types of specimens have been found to be complementary in practice. At high temperatures, where the vapor pressure of MgO is extremely high, vaporization and surface diffusion would deplete the limited amount of solute present in the thin film type of specimen. The vapor deposition technique has been used with great success in this temperature region (1600°C to 2500°C). At temperatures below 1600°C, the vapor

pressure of MgO is too small to produce a surface concentration sufficiently high relative to the 11.17% natural abundance of Mg^{26}O in the specimen. The reduced vapor pressure, however, eliminates the problem of film depletion and permits use of the sandwich type of specimen in this temperature region.

Two severe experimental problems were encountered in the preparation of satisfactory specimens. At high temperatures the vapor pressure of MgO is extremely large. It was necessary to devise some means for inhibiting vaporization of the specimen, protecting against volatilization of the small amount of isotope solute, and for protecting the sample from impurities derived from furnace elements. This was accomplished by encapsulating the entire diffusion specimen within a pressed cylinder of high purity MgO powder. The compact was found to sinter to high density during the diffusion annealing. This both entrapped the solute and protected the surfaces of the host crystal. At extremely high temperatures (greater than 2200°C) the vapor pressure of MgO was found to be too high to permit densification of the compact. Evidence was found for the partial reduction of the powder to Mg. The vapor deposition type of specimen was employed at these temperatures. It was found that while the compact eventually crumbled, it maintained the integrity of the specimen long enough for the host crystal to bond to the single crystal well and completely entrap the solute. Specimens have been satisfactorily prepared at temperatures up to 2500°C with this technique.

A second problem involved in the preparation of suitable sandwich specimens stems from the nature of the tracer employed. A sample usually has little natural radioactivity. Concentrations may, therefore, be detected down to very small levels if a radioisotope is employed as a tracer. In

the present work the diffusion of a stable isotope is studied. This isotope has a natural abundance in the host crystal which constitutes a "background" concentration of 11.17 atomic %. All concentrations used to establish a solute distribution must, therefore, be in excess of this level. Since the total amount of solute in the sandwich specimen is limited, concentration in the gradient decrease as the diffusion annealing proceeds, and the extent of the solute penetration increases. The total amount of isotope contained in the initial film must therefore be considerably larger than that used in experiments employing a radioisotope if final concentrations at acceptable penetrations into the specimen are to remain above the 11.17% background. Calculations presented in the preceding Interim Report demonstrated that initial film thicknesses of 5 to 10 microns were required in order to produce measurable gradients extending over 30 to 50 microns. Initial attempts to produce uniform films of the requisite thickness employed spraying of weakly acidic solutions or slurries of Mg^{26}O powders which were then sintered slightly in order to bond them to a prepared surface of the host crystal. The films produced were uniform, but invariably peeled from the surface when a thickness of $3/4$ micron was exceeded. The development of chemical transport techniques in another portion of the program eventually provided an ideal technique for application of the isotope films. A single crystal film of isotope tens of microns in thickness may now be deposited on the host crystal in epitaxial orientation in a matter of a few hours. The deposition is accomplished at times and temperatures (1000°C) small enough to be negligible compared to the conditions of the subsequent diffusion annealing. In addition to providing a single crystal film in intimate contact with the host crystal, this procedure has an additional important advantage in that

purification of the isotope is effected during the deposition procedure. This technique is presently being used in the preparation of all samples of the sandwich type.

4.3 Sample Analysis

After completion of a diffusion annealing in an argon atmosphere, sections are sequentially ground from the active surface of the single crystals. The sectioning is accomplished by attaching the crystal to a stainless steel cylinder which slides snugly within a second concentric cylinder of stainless steel. Grinding is performed on a Mo foil using diamond powder in a small amount of alcohol as an abrasive. Parallelism of the surface and lap during the grinding procedure is achieved by allowing the assembly to ride on supports concentric with the cylinders and of much greater diameter. The entire assembly rides on an optical flat. Thicknesses of material removed are determined by precision determination of the mass of the sample combined with an accurate measurement of its surface area. Sections of 2 micron thickness are readily obtained by this technique. Tallysurf measurements of surface roughness after removal of a section indicate that parallelism and flatness are maintained to within ± 0.25 micron.

Measurement of the isotopic composition of each section so removed is accomplished with the aid of mass spectrometry. The MgO grindings are placed in a tungsten Knudsen cell maintained at 1900°K . The vapor leaving its effusion orifice enters the ion source of a Bendix time-of-flight mass spectrometer, where it is ionized by electron impact. In initial measurements peaks at masses 24, 25, and 26 were scanned. The principal source of error in this procedure was fluctuations in beam

intensity arising from small changes in the temperature of the Knudsen cell. A supplementary detection system was therefore added to the spectrometer which permits simultaneous monitoring of the Mg^{24} and Mg^{26} peaks. A comparison of measured natural abundances of Mg isotopes with the reported values showed that this procedure provides isotopic compositions which are reliable to $\pm 1\%$.

4.4 Results

A total of twelve diffusion couples have presently been prepared at temperatures ranging from 1500° to 2050°C . All annealings were conducted in an argon atmosphere and with durations extending from 31 hrs., at the lower temperatures, to 6 hrs. Two types of magnesium oxide crystals were employed at each temperature. Crystals obtained from the Norton Company, Worcester, Massachusetts have been studied as crystals typical of the quality for which most measurements of transport in MgO have been made. Much purer crystals, obtained from W. & C. Spicer, Ltd., Cheltenham, England, have also been employed. The latter crystals reputedly contain of the order of 100 ppm impurity and represent the best quality crystals currently available. All problems associated with the preparation and analysis of samples have been satisfactorily resolved. Preparation of further specimens is proceeding on a routine basis.

A plot of a representative concentration gradient is presented in Figure 11, in which the inverse complementary error function of $(C-\text{Co})/(C_s-\text{Co})$ is plotted as a function of penetration into a single crystal of Norton MgO annealed for $16 \frac{1}{3}$ hrs. at 1750°C . A summary of the diffusion coefficients for Mg^{26} in MgO which have been obtained to date is presented in Table II.

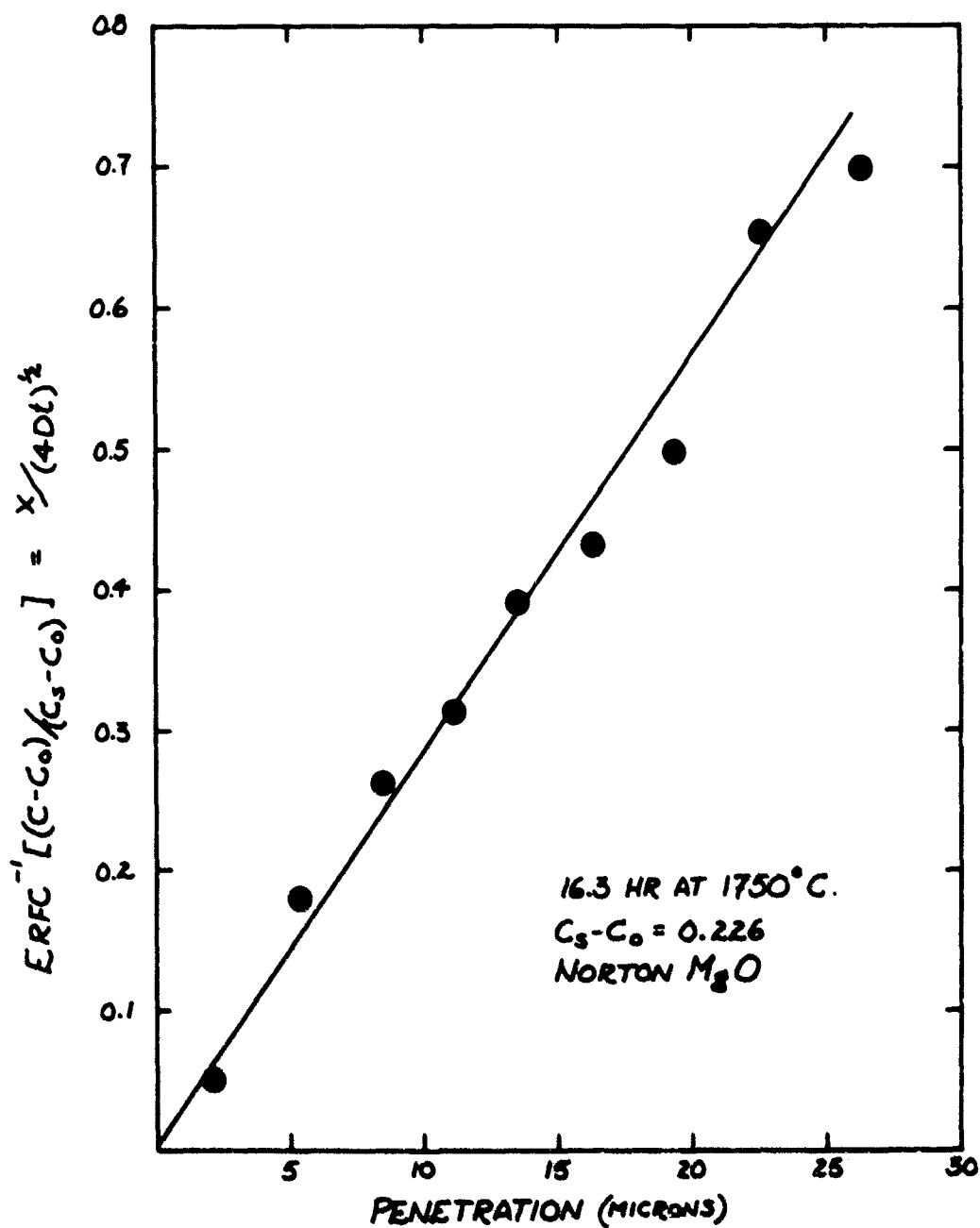


Figure 11. Plot of the inverse complementary error function of $(C - C_0)/(C_s - C_0)$ as a function of $Mg^{16}O$ penetration into a Norton MgO crystal annealed 16.3 hours at 1750°C in argon.

Table II
Diffusion Coefficients for Mg²⁶ in Single Crystal

<u>MgO in Argon Atmosphere</u>				
<u>Temperature</u> <u>°C</u>	<u>Time</u> <u>(hr)</u>	<u>Specimen Type</u>	<u>Crystal Type</u>	<u>D(cm²/sec)</u>
1600	16	Vapor deposition	Norton	$1.41 \cdot 10^{-11}$
1750	16.3	" "	Norton	$5.28 \cdot 10^{-11}$
1850	15.6	" "	Norton	$1.38 \cdot 10^{-10}$
1850	15.6	" "	Spicer	$5.87 \cdot 10^{-11}$

The diffusion coefficients are plotted as a function of reciprocal temperature in Figure 12 where they may be compared with the values previously reported by Lindner and Parfitt⁽¹⁾ for the temperature range 1400° - 1600°. We have not yet obtained enough data to permit a reliable measure of the activation energy for diffusion. However, the three diffusion coefficients obtained for the Norton crystals may tentatively be described by

$$D = 3.5 \cdot 10^{-3} \exp -(3.13 \text{ eV/kT})$$

The data of Lindner and Parfitt provide

$$D = 2.49 \cdot 10^{-1} \exp -(3.43 \text{ eV/kT}).$$

The diffusion coefficients of the present work are approximately an order of magnitude smaller at the temperatures at which the previous measurements had been made. Additional measurements may modify the diffusion parameters somewhat, but it appears that the high activation energy for Mg self-diffusion will be confirmed by the present study.

The analysis of only one specimen prepared with the high purity Spicer single crystals has been completed to date. The diffusion coefficient obtained for this crystal is a factor of 2 smaller than the corresponding

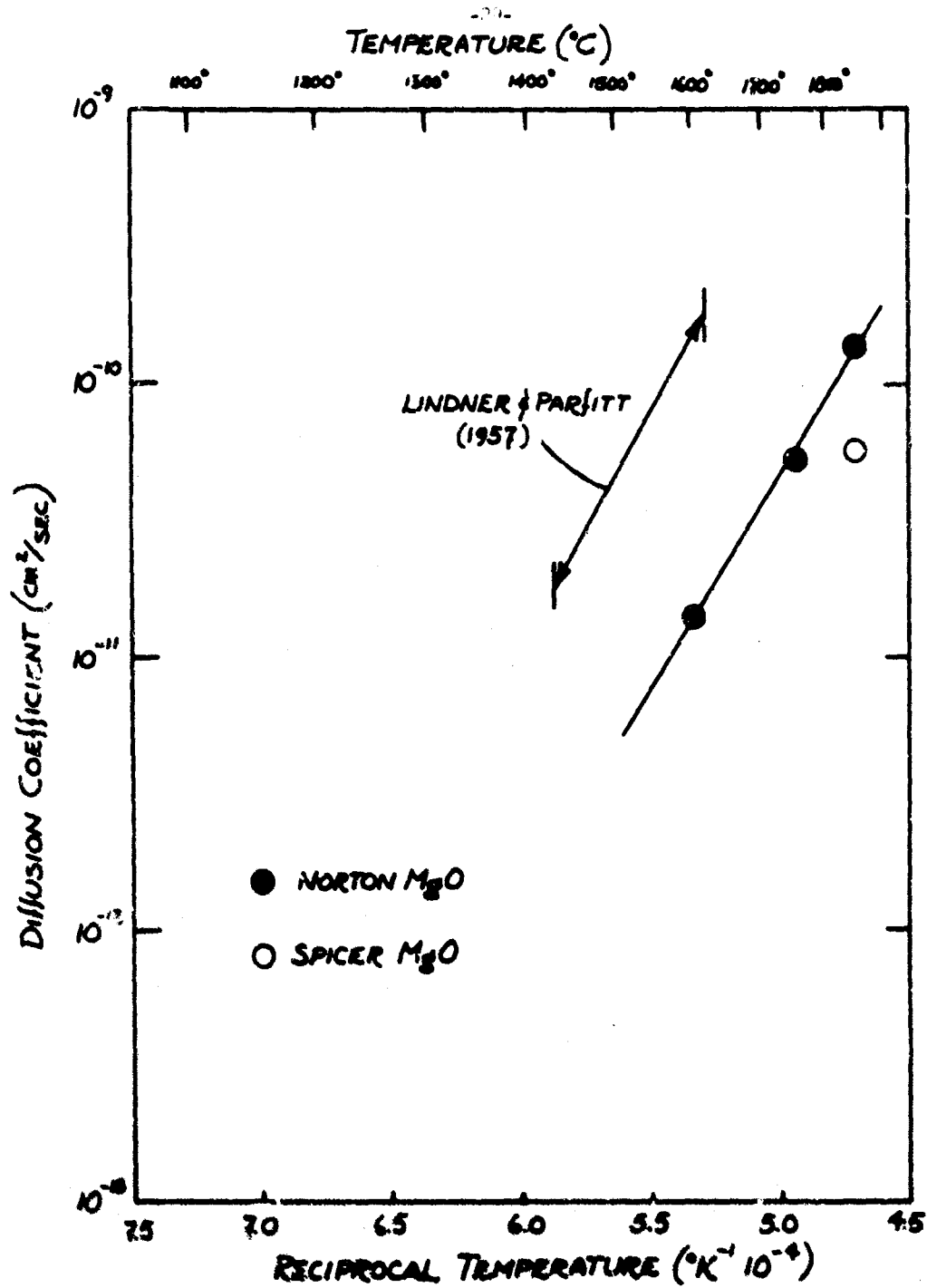


Figure 12. Plot of coefficients for Mg²⁺ self-diffusion in magnesium oxide as a function of reciprocal temperature.

value provided by the Norton crystal along with which the specimen had been prepared. Again, our conclusions must remain tentative until further data are obtained, but the markedly different diffusion coefficients would appear to indicate that diffusion in MgO is extrinsic at temperatures so far examined. The fact that the diffusion coefficient is smaller for the material with lower impurity cation content suggests that diffusion coefficients may be determined by cation impurities. A very different behavior has been found for impurity cation diffusion, as described in subsequent sections. This observation may provide the clue to the very different activation energies obtained for Mg^{2+} diffusion and for impurity cation diffusion.

V. IMPURITY CATION DIFFUSION AT HIGH TEMPERATURES

5.1 Introduction

Diffusion coefficients have been determined for a number of impurity cations in single crystal MgO. The majority of these studies have employed relatively impure crystal (1000 to 10,000 ppm impurity cation). Furthermore, none of these measurements have been extended to temperatures higher than 1850°C (0.66 of the melting temperature). At such temperatures there would be little possibility of intrinsic transport behavior.

The objective of this portion of the program is to extend measurement of diffusion rates for an impurity cation to as high a temperature as possible in an attempt to reveal a region of intrinsic transport. Measurements are being made with crystals of the highest purity currently available. For the purpose of comparison, a diffusion coefficient is determined under identical conditions with a crystal of lower purity which is typical of the material with which most data have been obtained.

5.2 Materials and Specimen Preparation

As in the measurements of Mg self-diffusion, diffusion coefficients have been determined for both Norton Co. and Spicer, Ltd. MgO single crystals. Ni^{2+} was selected as the impurity cation employed as a solute. Nickel oxide and magnesium oxide form a continuous series of solid solutions. The cation has the further advantage of having characteristic x-radiation for which the microprobe has high sensitivity.

The host crystal was cleaved into small plates (ca. 4 x 3 x 1 mm). Since only small areas of the sample are examined, it was not necessary to eliminate cleavage steps as in the case of the self-diffusion studies. Also, solute penetrations were found to be large (250 to 300 microns) compared to the extent of the surface damage incurred in cleavage. No surface preparation of the crystals was therefore deemed necessary.

Both the sandwich and vapor-deposition techniques of specimen preparation have been employed. The problems of sample protection described in connection with the self-diffusion studies were compounded by the still higher vapor pressure of the NiO solute. Many specimens were prepared at temperatures above the melting point of NiO (2090°C). All diffusion specimens were therefore encapsulated in a pressed cylinder of MgO powder. The annealings were conducted in an argon atmosphere.

In the sandwich technique the Ni^{2+} solute was applied to a cleaved surface of an MgO crystal as a film of nickel chloride a fraction of a micron in thickness. The chloride was subsequently converted to a layer of NiO by heating in air. Samples have been successfully prepared by this technique at temperatures ranging from 1900°C to 2200°C. At the latter temperature even the encapsulation procedure did not successfully retain the limited amount of solute which was present. The maximum

concentration of Ni^{2+} found in the gradient was only 0.06 atomic percent NiO, and a satisfactory analysis could not be completed.

During the present period of the program we have developed procedures for encapsulating vapor-deposition specimens. A small quantity of NiO powder is packed in a well machined in a portion of the same crystal to be employed as the host crystal. The latter crystal is placed over the well, and the entire assembly is then encapsulated in a pressed cylinder of MgO powder. As has been discussed in the preceding section, densification of the capsule was not achieved at temperatures above 2200°C . However, the specimen maintained integrity long enough to permit the host crystal to bond to the well and entrap the NiO solute. Specimens have been successfully prepared at temperatures up to 2460°C (0.88 of the melting temperature of MgO) with this procedure. An important advantage of the technique is that the host crystal is not in physical contact with the NiO solute, which, at these temperatures, is being maintained at a temperature several hundred degrees above its melting point.

5.3 Specimen Analysis

Determination of Ni^{2+} concentration gradients was accomplished with the aid of electron microbeam probe spectroscopy. Upon completion of the diffusion annealing the MgO capsule, if still intact, was sectioned to reveal the location of the diffusion specimen within the compact. A second cut was then made normal to the solute-coated interface to expose a surface for analysis. The surface was given a fine polish and coated with a thin film of carbon to render the sample conductive and prevent charge buildup during analysis. Intensities of $\text{NiK}\alpha$ fluorescent radiation were excited by bombardment with a 30 kv electron beam with a nominal diameter of one micron. All intensities are recorded relative to the intensity

obtained from a specimen of pure Ni in order to eliminate the effects of possible fluctuations in beam characteristics during analysis. The intensity ratios were converted to Ni^{2+} concentration by comparison with a set of intensity ratios obtained from a series of fine-grained sintered NiO-MgO solid solutions which were prepared as standards.

5.4 Results

Concentration gradients for sandwich-type specimens have been presented in preceding reports. A representative concentration gradient for a sample prepared by the vapor-deposition technique developed during the present portion of the program is presented in Figure 13. The inverse complementary error function of concentration divided by surface concentration is plotted as a function of penetration into a specimen of Norton MgO annealed for 4 hours at 2300°C in argon. The plot is linear, with slope equal to $(4Dt)^{-\frac{1}{2}}$ at all but low penetrations. The departure from linearity in this region is due to concentrations which are slightly too small. The effect may be attributed to either rounding of the edge of the crystal during polishing prior to the microprobe analysis (which would decrease the measured intensity) or, more probably, a loss of NiO by vaporization from the surface of the crystal during the final portion of the diffusion annealing. The effect is not considered significant, and does not interfere with the evaluation of a diffusion coefficient.

The diffusion coefficients obtained to date are summarized in Table III. Measurement of the concentration gradient was, for some specimens, performed at more than one location at the surface of the sample. The diffusion coefficient derived from each analysis is included in Table III, and serves to indicate the reliability of the determination. Analysis

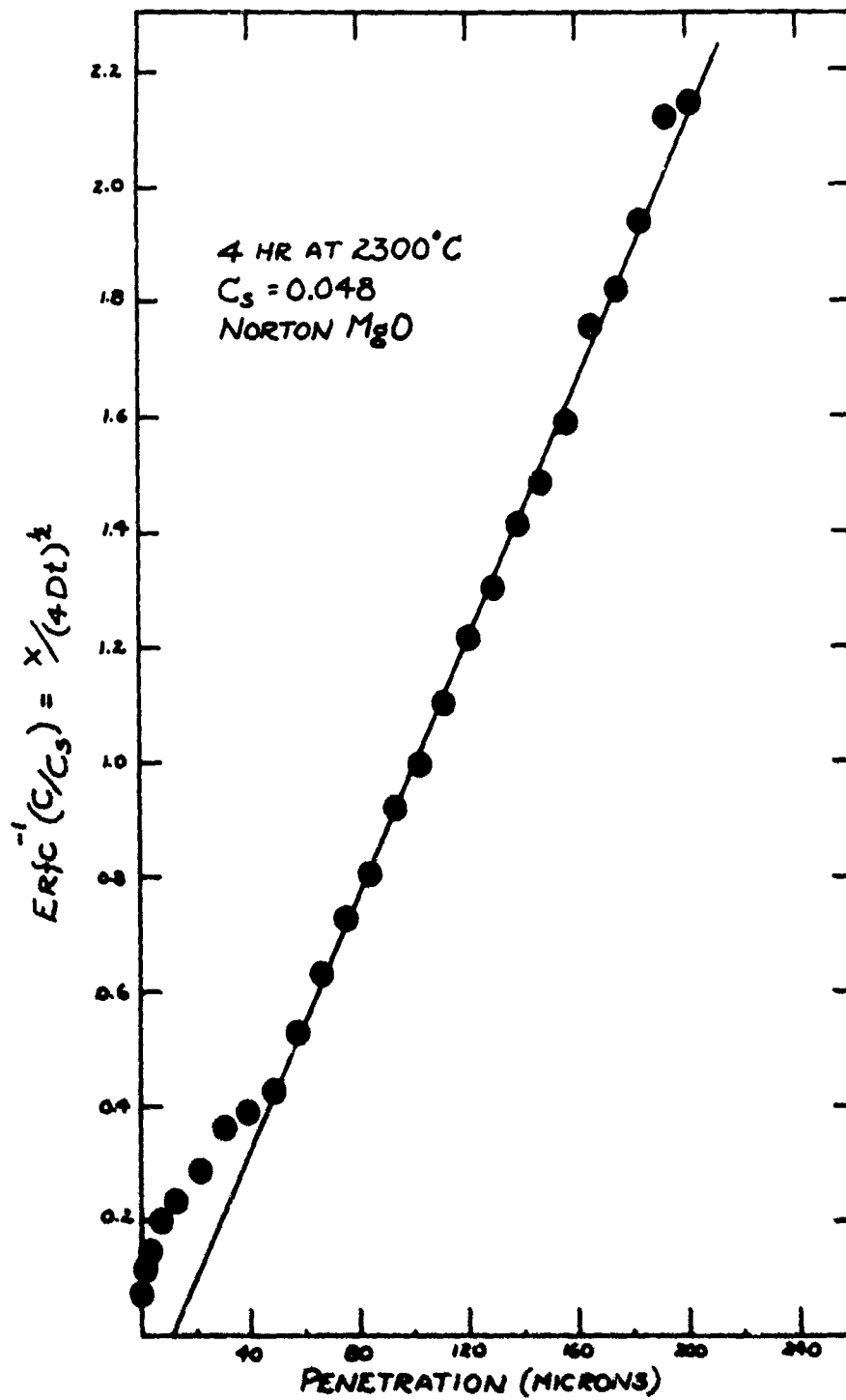


Figure 13. Plot of the inverse complementary error function of C/C_s for Ni * penetration into a Norton MgO sinter sintered 4 hours at 2300°C in argon.

TABLE III
Diffusion Coefficients for Ni^{2+} in Single Crystal MgO at High Temperatures

Diffusion Coefficient (cm^2/sec)

Sample Number	Temp. ($^{\circ}\text{C}$)	Time (hr)	Technique	Norton MgO			Spicer MgO			Extrapolation of low temperature data (Wuensch & Vacillos, 1962)
				Crystal 1	Crystal 2	Average	Crystal 1	Crystal 2	Average	
N11	1900	17.5	Sandwich	$1.08 \cdot 10^{-10}$ $1.66 \cdot 10^{-10}$	$2.30 \cdot 10^{-10}$ $2.50 \cdot 10^{-10}$	$1.89 \cdot 10^{-10}$	$1.98 \cdot 10^{-10}$ $2.60 \cdot 10^{-10}$	$(4.62 \cdot 10^{-10})$ $2.64 \cdot 10^{-10}$	$2.41 \cdot 10^{-10}$	$2.47 \cdot 10^{-10}$
N14	2000	7.5	Sandwich	$3.06 \cdot 10^{-10}$	$2.12 \cdot 10^{-10}$	$2.60 \cdot 10^{-10}$	$1.79 \cdot 10^{-10}$ $9.03 \cdot 10^{-10}$	$4.66 \cdot 10^{-10}$ $5.32 \cdot 10^{-10}$	$5.20 \cdot 10^{-10}$	$4.05 \cdot 10^{-10}$
N15	2100	7.7	Sandwich	$9.86 \cdot 10^{-10}$	-	$9.86 \cdot 10^{-10}$	$1.65 \cdot 10^{-9}$	-	$1.65 \cdot 10^{-9}$	$6.36 \cdot 10^{-10}$
N16	2200	5.0	Sandwich	$2.9 \cdot 10^{-9}$ $5.9 \cdot 10^{-9}$	-	$4.4 \cdot 10^{-9}$ *	-	-	-	$9.61 \cdot 10^{-10}$
N17	2300	4.0	Vapor-Deposition	$1.39 \cdot 10^{-9}$	-	$1.39 \cdot 10^{-9}$	-	-	-	$1.42 \cdot 10^{-9}$
N18	2460	1.0	Vapor-Deposition	$7.77 \cdot 10^{-9}$	$6.59 \cdot 10^{-9}$	$7.18 \cdot 10^{-9}$	$8.49 \cdot 10^{-9}$	-	$8.49 \cdot 10^{-9}$	$2.45 \cdot 10^{-9}$

*E time concentrations too low to provide a satisfactory gradient.

of two different samples of the same material were performed at several temperatures. Comparison of the diffusion coefficients obtained in these instances serves to indicate the variation in diffusion rates from sample to sample for a given material. Table III further includes the values of the diffusion coefficients obtained from extrapolation of data obtained from Norton crystals in the temperature range 1000° to 1850°C ⁽⁵⁾.

The diffusion coefficients for Ni^{2+} in MgO are plotted as a function of reciprocal temperature in Figure 14. For temperatures up to about 2300°C , the diffusion coefficients agree satisfactorily with an extrapolation of the low temperature results previously obtained⁽⁵⁾. A completely unexpected result, however, is that in every instance the Spicer crystals, which have lower dislocation densities and significantly smaller concentration impurity cation contents, provided a larger diffusion coefficient. This is the reverse of the situation which appears to be the case in our study of Mg self-diffusion! In any event, it is not the cation impurity content which governs Ni^{2+} diffusion rates in single crystal MgO .

Another interesting feature of Figure 14 is that at 2460°C , the highest temperature to be examined, both the Spicer and Norton MgO crystals provide a diffusion coefficient which is larger than the extrapolated value. This result must be interpreted with caution. Samples are extraordinarily difficult to prepare at these temperatures. Diffusion coefficients are not only subject to increased error, but the shorter duration permitted for the diffusion annealing results in the warm-up time being a more appreciable fraction of the annealing time itself. It thus becomes increasingly difficult to assign a precise time and temperature to the conditions of specimen preparation. Nevertheless, the four-fold increase

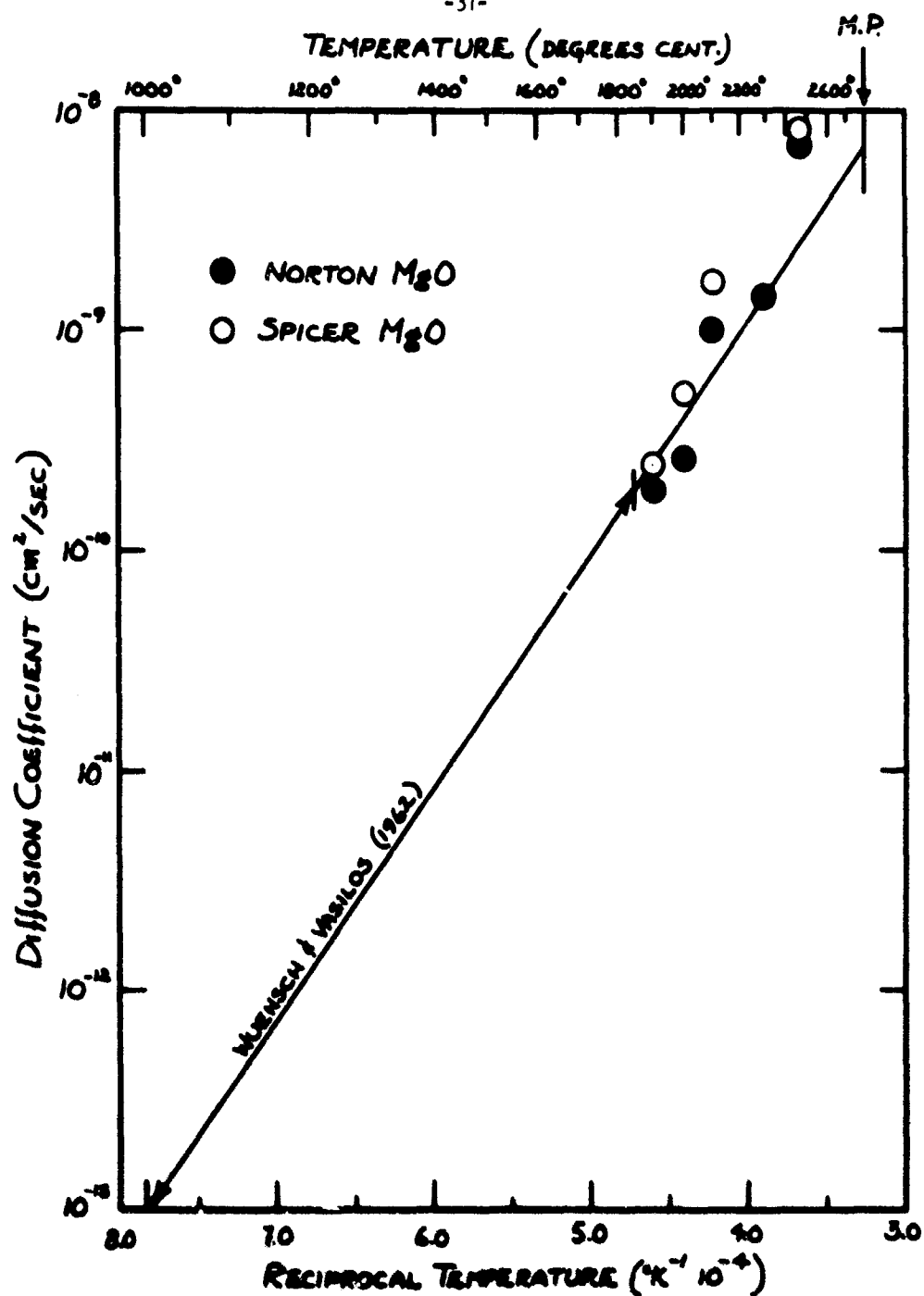


Figure 14. Plot of diffusion coefficients for Ni^{2+} in single crystal MgO as a function of reciprocal temperature.

in diffusion coefficient at 2460°C is more than can be accounted for by experimental error. It is felt that at this temperature, diffusion is possibly beginning to be controlled by a different mechanism. It would be desirable to confirm this through analysis of a sample prepared at still higher temperatures. This will not be attempted, however. In addition to the experimental difficulties referred to above, a still larger fraction of the NiO-MgO solid solution series would be above the solidus of the system. The study will be concluded with the preparation of additional pairs of samples at 2300° and 2400°C . However, the implication of the above results is that the transition temperature of a crystal of slightly improved quality might be shifted down to a more accessible temperature range. Development of techniques for crystal growth by chemical transport has, as described above, progressed to the point where a crystal suitable for diffusion measurements may be prepared. An attempt will shortly be made to prepare a diffusion specimen with one of these crystals.

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13. ABSTRACT Progress is described in a program intended to clarify the nature of mass transport in MgO, a ceramic oxide. The objectives of the program are to (1) prepare single crystals of purity and perfection superior to those presently available, (2) develop techniques permitting study of stable isotope diffusion and apply them to cation self-diffusion in MgO, and (3) extend measurement of impurity cation and cation self-diffusion coefficients to temperatures as close to the melting point of MgO as possible, in an attempt to reveal a region of intrinsic diffusion. Measurements of cation self-diffusion rates obtained for MgO are tentatively represented by a pre-exponential term, D_0 , equal to $4.5 \cdot 10^{-1}$ cm ² /sec and an activation energy of 3.13 eV, confirming a surprisingly large value reported elsewhere on the basis of data obtained over a very limited temperature range. Diffusion rates in high purity crystals are smaller by a factor of 3, and transport is interpreted as extrinsic. Measurements of Ni ²⁺ diffusion in MgO have been extended to 2400°C. Data agree well with an extrapolation of measurements performed at lower temperatures. Surprisingly, diffusion in high purity crystals is more rapid. At 2400°C there is indication of a possible change in the mechanism of diffusion.		

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